APPLICATION FOR UNITED STATES PATENT

SLURRY HYDROCARBON SYNTHESIS WITH LIQUID HYDROISOMERIZATION IN THE SYNTHESIS REACTOR

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SLURRY HYDROCARBON SYNTHESIS WITH LIQUID HYDROISOMERIZATION IN THE SYNTHESIS REACTOR

5   BACKGROUND OF THE DISCLOSURE

Field of the Invention

[0001]   The invention relates to a slurry hydrocarbon synthesis process with

10   hydrocarbon hydroisomerization in the synthesis reactor. More particularly the invention relates to a slurry Fischer-Tropsch hydrocarbon synthesis process, wherein the synthesized hydrocarbon slurry liquid is hydroisomerized in the synthesis reactor, by reacting with hydrogen in the presence of a monolithic hydroisomerization catalyst in a gas lift reactor at least partially immersed in the

15   slurry.

Background of the Invention

[0002]   The slurry Fischer-Tropsch hydrocarbon synthesis process is now well

20   known and documented, both in patents and in the technical literature. This process comprises passing a synthesis gas, which comprises a mixture of H_2 and CO, up into a hot reactive slurry comprising synthesized hydrocarbons which are liquid at the synthesis reaction conditions and in which is dispersed a particulate Fischer-Tropsch type of catalyst. The H_2 and CO react in the presence of the

25   catalyst and form hydrocarbons. The hydrocarbon liquid is continuously or intermittently withdrawn from the synthesis reactor and pipelined to one or more downstream upgrading operations. The upgraded products may include, for example, a syncrude, various fuels and lubricating oil fractions and wax. The downstream upgrading includes fractionation and conversion operations, typically comprising hydroisomerization, in which a portion of the molecular

30   typically comprising hydroisomerization, in which a portion of the molecular

structure of at least some the hydrocarbon molecules is changed. It would be an improvement if the synthesized hydrocarbon slurry liquid could be at least partially hydroisomerized to reduce its pour and melt points within the synthesis reactor, to make it more transportable by pipeline before it is transferred to

5   operations downstream and without the need for a separate hydroisomerization facility.

SUMMARY OF THE INVENTION

10   [0003]   The invention relates to a slurry Fischer-Tropsch hydrocarbon synthesis process in which the synthesized hydrocarbon slurry liquid is hydroisomerized in the synthesis reactor by circulating it up through one or more gas lift reactors at least partially immersed in the synthesis slurry, in which the liquid reacts with hydrogen in the presence of a hydroisomerization catalyst and

15   preferably a monolithic hydroisomerization catalyst, to hydroisomerize the liquid which is then passed back into the slurry body in the synthesis reactor. The slurry liquid, which comprises synthesized hydrocarbons that are liquid at the synthesis reaction conditions, comprises mostly normal paraffins and the hydroisomerization reduces its pour and melt points, thereby making it more

20   pumpable and pipelinable. By gas lift reactor (hereinafter "lift reactor") is meant a reactor inside the synthesis reactor immersed in the slurry body therein, and wherein circulation of slurry from the surrounding slurry body, up into its interior and back out and into the surrounding slurry body, is achieved all or mostly by the lift action of hydrogen treat gas passed into it. By immersed in the

25   slurry body in the practice of the invention, is meant wholly or mostly immersed in it. The lift reactor may comprise a simple substantially vertically oriented, hollow fluid conduit, such as a pipe open at its top and bottom and containing a hydroisomerization catalyst in its interior, along with means for injecting the hydrogen treat gas into its interior. The lift reactor(s) may be regarded as a form

of lift tube or riser reactor. The process comprises contacting hot slurry from the slurry body with means for removing gas bubbles, and preferably both gas bubbles and particulate solids from it, to produce at least a gas bubble reduced slurry which, along with a hydrogen treat gas, is then passed up into the one or

5 more gas lift reactors in which the slurry hydrocarbon liquid is at least partially hydroisomerized and then passed back into the slurry body. The hydroisomerizing catalyst located in the interior of the gas lift reactor comprises the hydroisomerization zone which is surrounded by the slurry body, but it isolated from direct contact with it. This enables hydroisomerizing the slurry

10 liquid (i) inside the synthesis reactor and (ii) while the synthesis reactor is producing hydrocarbons, but without interfering with the hydrocarbon synthesis reaction. The concentration of hydroisomerized hydrocarbon liquid in the synthesis reactor continues to increase until equilibrium conditions are reached. When the synthesis reactor reaches equilibrium, it is possible for the slurry

15 liquid being removed from it to comprise mostly hydroisomerized hydrocarbons of reduced pour point. In some cases, no further hydroisomerization of the liquid hydrocarbon product withdrawn from the synthesis reactor is necessary. Thus, the process of the invention will reduce and in some cases even eliminate the need for a separate, stand-alone hydroisomerization reactor and associated

20 equipment, downstream of the synthesis reactor. If a downstream hydroisomerization reactor is needed, it will be smaller than it would be if the synthesized hydrocarbon liquid passed into it was not at least partially hydroisomerized. While all of the hydroisomerized hydrocarbon liquid is typically returned back into the surrounding slurry body in the synthesis reactor

25 with which it mixes, in some embodiments a portion of the hydroisomerized liquid may be passed from the lift reactor, directly out of the syntheses reactor to downstream operations.

[0004] The gas bubble and preferably the slurry gas bubble and particulate solids removal means is also located in the slurry body in the synthesis reactor and may comprise the same or separate means. While various filtration means may be used to separate the slurry liquid from at least a portion of the catalyst

5   and any other particles, before it is passed up into the hydroisomerization zone, in the practice of the invention the use of filtration means may be avoided by using known slurry solids reducing means that do not employ filtration. Simple gas bubble and solids removal means suitable for use with the present invention and which operate on density differences and gravity are known and disclosed

10   in, for example, U.S. patents 5,866,621 and 5,962,537, the disclosures of which are incorporated herein by reference. Simple gas bubble removing means are disclosed in U.S. patents 5382,748; 5,811,468 and 5,817,702, the disclosures of which are also incorporated herein by reference. In these patents, the gas bubble and the gas bubble and solids removal means are immersed in the slurry body

15   and comprise the slurry entrance at the top of a downcomer, while the simple gas bubble removal means are located at the top of a downcomer and the bottom of a rejuvenation tube, which is a form of lift reactor. In the '468 patent, a lift reactor rejuvenation tube is fed a gas bubble-reduced slurry by means of a downcomer immersed in the slurry, which turns up into the rejuvenation tube. Gas bubble

20   removal increases the density of the slurry, so that the density of gas bubble-reduced slurry passing from the slurry body in the synthesis reactor into the bottom of the lift reactor is denser than the surrounding slurry body. This acts somewhat against the lift action of the hydrogen treat gas passed into the lift reactor. Therefore, in some cases it is preferred that the gas bubble removal take

25   place as high up in the slurry body as possible, to provide a density-difference hydraulic driving force, in addition to the lift action of the hydrogen or hydrogen treat gas passed or injected into the hydroisomerization zone, to assist slurry circulation up through and out of the lift reactor. Such means may be located proximate or part of the entrance to a downcomer means or conduit which passes

the densified, gas bubble or gas bubble and solids-reduced slurry down and into the bottom of the lift reactor. Removing gas bubbles from the slurry prior to hydroisomerization also reduces its CO and water vapor content, which could otherwise react with the hydroisomerization hydrogen and also adversely effect

5   the hydroisomerization catalyst. A monolithic hydroisomerization catalyst having substantially vertical fluid flow channels and a minimal solid cross-sectional area perpendicular to the flow direction of the fluid minimizes the pressure drop of the fluid flowing down and across the catalyst surface. Removing catalyst and other solid particles, such as inert heat transfer particles,

10   from the slurry upstream of the hydroisomerization zone, reduces scouring of the monolithic catalyst, plugging of the hydroisomerization reaction zone and also reduces the liquid phase viscosity.

[0005]   The invention comprises a slurry Fischer-Tropsch hydrocarbon

15   syntheses process in which synthesized hydrocarbon slurry liquid is hydroisomerized in the synthesis reactor during hydrocarbon synthesis, by circulating slurry from the slurry body in the synthesis reactor up through a hydroisomerization zone, in a lift reactor immersed in the slurry body, in which the slurry hydrocarbon liquid reacts with hydrogen in the presence of a

20   hydroisomerization catalyst. Slurry circulation between the downcomer reactor and slurry body is achieved by contacting a portion of slurry from the slurry body with gas bubble removal means to densify the slurry. At least a portion of the slurry liquid is hydroisomerized which reduces its pour point. The hydroisomerized slurry leaves the lift reactor and all or most of it passes back

25   into the surrounding slurry body with which it mixes. Preferably the hydroisomerization catalyst comprises a monolithic catalyst and at least a portion of both solids and gas bubbles are removed from the slurry before it contacts the hydroisomerization catalyst. More specifically the invention comprises a hydrocarbon synthesis process, which includes hydroisomerizing

hydrocarbon liquid produced by the synthesis reaction while the hydrocarbon liquid is being produced from a synthesis gas, the process comprising the steps of:

5   a) passing a synthesis gas comprising a mixture of H_2 and CO into a slurry body in a slurry Fischer-Tropsch hydrocarbon synthesis reactor, in which the slurry comprises gas bubbles and a particulate hydrocarbon synthesis catalyst in a slurry hydrocarbon liquid;

10   (b) reacting the H_2 and CO in the presence of the catalyst at reaction conditions effective to form hydrocarbons, a portion of which are liquid at the reaction conditions and comprise the slurry hydrocarbon liquid;

     (c) contacting a portion of the slurry from the slurry body with

15   means for removing gas bubbles, to form a slurry reduced in gas bubbles;

     (d) passing a hydrogen treat gas and the gas bubble reduced slurry into a hydroisomerizing zone in one or more lift reactors immersed in the slurry body in the synthesis reactor, in which the hydrogen and hydrocarbon slurry

20   liquid react in the presence of a preferably monolithic hydroisomerization catalyst to form a hydrocarbon liquid of reduced pour point, and

     (e) passing all or a portion of the pour point reduced liquid back into the surrounding slurry body.

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BRIEF DESCRIPTION OF THE FIGURES

[0006]   Figure 1 is a simple schematic flow diagram of a hydrocarbon synthesis reactor containing a hydroisomerization zone within, according to one embodiment of the invention.

[0007]   Figure 2 is a plot of hexadecane conversion as a function of temperature in the presence of a monolithic hydroisomerization catalyst in a pilot plant tubular reactor

[0008]   Figure 3 is a graph illustrating hexadecane hydroisomerization selectivity over a monolithic hydroisomerization catalyst in a pilot plant tubular reactor.

DETAILED DESCRIPTION

[0009]   The waxy slurry liquid synthesized in the reactor will typically comprise $500^{\circ}F+$ hydrocarbons, with most having an initial boiling point in the $650\text{-}750^{\circ}F+$ range. The end boiling point will be at least $850^{\circ}F$, preferably at least $1050^{\circ}F$ and even higher ($1050^{\circ}F+$). This liquid also comprises mostly (more than 50 wt. %), typically more than 90 %, preferably more than 95 % and more preferably more than 98 wt. % paraffinic hydrocarbons, most of which are normal paraffins, and this is what is meant by "paraffinic" in the context of the invention, particularly when the hydrocarbon synthesis catalyst comprises a cobalt catalytic component. The exact boiling range, hydrocarbon composition, etc, are determined by the catalyst and process variables used for the synthesis. It has negligible amounts of sulfur and nitrogen compounds (e.g., less than 1 wppm). Slurry liquids having these properties and useful in the process of the invention have been made using a slurry Fischer-Tropsch process with a catalyst

having a catalytic cobalt component. In the practice of the invention, it is preferred that the slurry Fischer-Tropsch hydrocarbon synthesis catalyst comprise a catalytic cobalt or iron component. It is also preferred that the synthesis reaction have a Schulz-Flory alpha of at least 0.90, as higher molecular

5   weight hydrocarbons are preferred in most cases. The gas bubbles in the slurry comprise synthesis gas, vapor and gaseous products of the synthesis reaction, such as C_1-C_4 hydrocarbons, and especially methane, CO_2 and water vapor. The hydroisomerization catalyst is adversely effected by water vapor. Therefore, in addition to densifying the slurry, gas bubble removal is also beneficial to the

10   downstream hydroisomerizing catalyst.

[0010]   The hydroisomerization catalyst will have a both a hydrogenation/dehydrogenation function and an acid hydrocracking function for hydroisomerizing the normal paraffinic hydrocarbons in the slurry hydrocarbon

15   liquid. The hydrocracking functionality of the catalyst results in the conversion of some of the waxy slurry liquid to lower boiling material. The hydroisomerization temperature and pressure will be substantially the same as that in the hydrocarbon synthesis reactor, unless means are employed to heat or cool the gas reduced slurry passing up through the lift reactor. The pressure in

20   the hydroisomerization zone will be substantially the same as that in the synthesis reactor, which is about 80-600 psig. U.S. patent 5,268,344, the disclosure of which is incorporated herein by reference, discloses means for adjusting the temperature in a vertical catalyst rejuvenation draft tube immersed in the slurry and these means may also be used to adjust the temperature in the

25   interior of the lift reactor in the practice of the present invention. However, this will mean that the heat exchange means in the slurry synthesis reactor used to remove some of the exothermic heat of the synthesis reaction, will also have to remove the additional heat added in the hydroisomerization zones(s), in the case of heat addition into these zones to increase the hydroisomerization temperature

above that of the synthesis temperature. This may not be feasible or desirable. Thus, while hydroisomerization is broadly achieved at reaction temperatures ranging from 300-900°F and preferably 550-750°F, the temperature and pressure in a slurry hydrocarbon synthesis reactor will typically range from 320-

5   600°F and 80-600 psig. The hydrogen treat gas rate will be from 500-5000 SCF/B, with a preferred range of 2000-4000 SCF/B. By hydrogen treat gas is meant all hydrogen or preferably at least about 60 vol. % hydrogen and an inert diluent gas, such as argon or methane. Excess hydrogen is employed during the hydroisomerization to insure an adequate hydrogen partial pressure and to

10   prevent any CO remaining in the upflowing slurry from adversely effecting the hydroisomerization reaction and catalyst. The hydroisomerization catalyst comprises one or more Group VIII catalytic metal components supported on an acidic metal oxide support to give the catalyst both a hydrogenation function and an acid function for hydroisomerizing the hydrocarbons. At the relatively lower

15   hydroisomerizing temperatures, such as the temperature in the slurry hydrocarbon synthesis reactor, the catalytic metal component will typically comprise a Group VIII noble metal, such as Pt or Pd, and preferably Pt. However, if means are employed in the practice of the invention to raise the temperature in the hydroisomerization zone to sufficiently high levels, it will

20   typically be preferred that the catalytic metal component comprise one or more less expensive non-noble Group VIII metals, such as Co, Ni and Fe, which will typically also include a Group VIB metal (e.g., Mo or W) oxide promoter. Irrespective of which Group VIII metal component is used, the catalyst may also have a Group IB metal, such as copper, as a hydrogenolysis suppressant. The

25   Groups referred to herein refer to Groups as found in the Sargent-Welch Periodic Table of the Elements copyrighted in 1968 by the Sargent-Welch Scientific Company. The cracking and hydrogenating activity of the catalyst is determined by its specific composition, as is known. In a preferred embodiment the catalytically active metal comprises cobalt and molybdenum. The acidic oxide

support or carrier may include silica, alumina, silica-alumina, silica-alumina-phosphates, titania, zirconia, vanadia, and other Group II, IV, V or VI oxides, as well as Y sieves, such as ultra stable Y sieves. Preferred supports include silica, alumina and silica-alumina and, more preferably silica-alumina in which the

5   silica concentration in the bulk support (as opposed to surface silica) is less than about 50 wt. %, preferably less than 35 wt. % and more preferably 15-30 wt. %. Lower hydroisomerization temperatures require a more active catalyst and therefore a more acidic support than do higher temperatures. In such cases, for example, a conventional silica-alumina support component may not have enough

10   acidity and crystalline alumina-silicas will be preferred, such as beta sieves in which the silica to alumina ratio ranges from less than 50:1 to less than 20:1. As is known, if the support is alumina, small amounts of fluorine or chlorine are often incorporated into it to increase the acid functionality. However, in the process of the invention, the use of halogens in the catalyst is to be avoided, to

15   prevent potential impairment of the hydrocarbon synthesis catalyst.

[0011]   If temperatures higher than those in the synthesis reactor are employed in the lift reactor, a non-noble metal hydroisomerization catalyst that is particularly preferred in the practice of the invention comprises both cobalt and

20   molybdenum catalytic components supported on an amorphous, low silica alumina-silica support, and most preferably one in which the cobalt component is deposited on the support and calcined before the molybdenum component is added. This catalyst will contain from 10-20 wt. % MoO_3 and 2-5 wt. % CoO on an amorphous alumina-silica support in which the silica content ranges from

25   20-30 wt. % of the support. This catalyst has been found to have good selectivity retention and resistance to deactivation by oxygenates typically found in Fischer-Tropsch produced waxy feeds. The addition of a copper component suppresses hydrogenolysis. The preparation of this catalyst is disclosed in, for

example, U.S. patents 5,757, 920 and 5,750,819, the disclosures of which are incorporated herein by reference.

[0012]   Hydroisomerization can be enhanced by using noble metal containing catalysts in at least one hydroisomerization zone within the downcomer reactor and non-noble metal containing catalysts in at least one other hydroisomerization zone within the downcomer reactor.

[0013]   Monolithic catalysts are known for automotive exhausts and for chemical reactions as is shown, for example, in an article by Crynes, et al., "Monolithic Froth Reactor: Development of a novel three-Phase Catalytic System", AIChE J, v. 41, n. 2, p. 337-345 (Feb. 1995). A corrugated type of monolithic catalyst has even been suggested for Fischer-Tropsch hydrocarbon synthesis (GB 2,322,633 A). Basically, monolithic catalysts comprise a ceramic or metal support structure of a desired shape, with a catalyst applied to its surface. The monolith may be a metal foam or may be prepared from the catalyst composition itself or from the catalyst support, e.g., molecular sieves, with the catalytic metal(s) deposited onto the monolith support. In this latter case, monolith attrition will still leave catalyst available for the hydroisomerization reaction. Preferred channel sizes for monoliths are in the range > 300 μm and less than 600 μm. Very high strength monolithic catalysts may be fabricated from a metal foundation, over which is applied a suitable ceramic and then the catalyst. The catalytic material may be a finished catalyst which has been ground to a small particle size, slurried in an appropriate liquid, such as water or an organic liquid, with the slurry then applied to the monolithic support surface as a wash coat and calcined. It is also possible to apply one or more applications of catalytic precursor materials to the ceramic support by impregnation or incipient wetness, followed by drying and calcining. In the practice of the invention, a monolithic catalyst having a minimal solid cross-

sectional area perpendicular to the fluid flow direction is preferred, to minimize the pressure drop of the fluid flowing across the catalytic surface. Such catalysts will not be limited to containing substantially longitudinal and parallel fluid flow channels. However, since pressure drop across the catalyst is important, this

5 must be taken into consideration. Micron size channel openings or openings on the order of a few microns will not be large enough for this application but openings generally exceeding 300 microns would be acceptable. Suitable catalyst shapes for providing a low pressure drop include an open cell foam structure, and configurations having a low cross-sectional area perpendicular to

10 the fluid flow direction may also be used. Such shapes will include, for example, elongated star shapes, with and without an outer peripheral wall, corrugated constructions, with longitudinal channels parallel to the fluid flow direction, a honeycomb containing a plurality of open-ended flow channels substantially parallel to the fluid flow direction and the like. Many of these

15 shapes may be extruded from a preceramic paste, dried and then fired to the green or fully fired to the final state, to provide the foundation for the catalyst material. Still further, all or some of the monolithic catalysts used in the hydroisomerization zone may be shaped in the form of a low pressure drop static mixer, such as a Kenics® static mixer in the form of slightly twisted or spiral-

20 shaped metal strips. A monolithic catalyst having this shape may be prepared by applying a ceramic over a twisted metal strip and then applying or forming the catalyst on the ceramic. The advantage of this is to provide more intimate mixing of hydrogen and liquid and to prevent stratification of the gas and liquid flows as they flow up through the hydroisomerizing zone.

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[0014]   In the practice of the invention, the hydroisomerization zone in the lift reactor will preferably comprise a plurality of monoliths vertically arrayed on top of each other in the hydroisomerization zone. For example, in the case of a lift reactor comprising an elongated and substantially vertical conduit, such as a

pipe, a plurality of cylindrical monoliths may be vertically arranged or arrayed inside the lift reactor conduit to form the hyroisomerization zone. The cross-sectional area of the catalyst monoliths perpendicular to the direction of fluid flow will typically proximate that of the interior of the conduit. It is preferred that there be vertical spaces between at least some of the monoliths, to prevent stratification of the gas and liquid as they flow up through the zone. More preferably, a low pressure drop static mixer, such as a Kenics® static mixer will be placed in the space between at least some of the arrays, to insure adequate mixing and remixing of the hydrogen treat gas and slurry liquid, as they flow up through the zone. Still further, as mentioned above, some or all of the catalyst monoliths themselves may be in the form of a low pressure drop static mixer, to insure good mixing and low pressure drop. It is preferred to inject the hydrogen or hydrogen treat gas into the hydroisomerization zone via a plurality of gas injection means, vertically spaced apart along the hydroisomerization zone. This will help to insure good mixing of the upflowing fluid and the hydrogen. It is more preferred that the hydrogen be injected into such spaces upstream of one or more low pressure drop static mixers in the hydroisomerization zone, to mix the injected gas into the upflowing liquid at each gas injection point. The invention will be further understood with reference to the Figures.

[0015] Referring to Figure 1, a slurry hydrocarbon synthesis reactor 10 is shown as comprising a cylindrical vessel 12 with a synthesis gas feed line 14 at the bottom and a gas product line 16 at the top. A synthesis gas comprising a mixture of H_2 and CO is introduced into the plenum space 22 at the bottom of the vessel via feed line 14 and then injected up through a gas injection means briefly illustrated by dashed line 18 and into the slurry body 20, which is a three-phase slurry comprising bubbles of the uprising synthesis gas, and vapor and gas products of the synthesis reaction, along with solid particles of a Fischer-Tropsch catalyst in a hydrocarbon slurry liquid which comprises synthesized

hydrocarbons that are liquid at the temperature and pressure in the reactor. Suitable gas injection means comprises a plurality of gas injectors horizontally arrayed across and extending through an otherwise gas and liquid impermeable, horizontal tray or plate, as is disclosed for example, in U.S. patent 5,908,094 the

5 disclosure of which is incorporated herein by reference. The H_2 and CO in the slurry react in the presence of the particulate catalyst to form predominantly paraffinic hydrocarbons, most of which are liquid at the reaction conditions, particularly when the catalyst includes a catalytic cobalt component. Unreacted synthesis gas and gas products of the hydrocarbon synthesis reaction rise up and

10 out the top of the slurry and into the gas collection space 24 in the top of the reactor, from where they are removed from the hydrocarbon synthesis reactor as tail gas via line 16. A filter means immersed in the slurry, which is simply indicated by box 26, separates the hydrocarbon liquids in the reactor from the catalyst particles and passes the synthesized and hydroisomerized hydrocarbon

15 liquid out of the reactor via line 28. Filter 26 may be fabricated of sintered metal, wound wire and the like to separate the liquid product from the particulate solids in the slurry, and the slurry liquid removed via line 28 is typically sent to further processing or sold as a highly refined syncrude of reduced pour point. Not shown is means for overhead removal and replacement of the filter. An

20 internal lift reactor 30 is shown as a vertical, hollow fluid conduit wholly immersed in the surrounding slurry body 20, with its open top 34 just above the top of the slurry body, so that the hydroisomerization offgas does not pass into it. If desired, the hydroisomerization reaction offgas can be separately recovered or passed directly into line 16, as is disclosed in U.S. patent 5,811,363 the

25 disclosure of which is incorporated herein by reference. In the embodiment shown, a gas bubble-reducing downcomer 40 is used to remove gas bubbles from the slurry and feed it down through space between the inner downcomer wall surface and the outer surface of a filter means 42, which separates solid particles from the slurry liquid. The gas bubble reduction is achieved by an

upwardly opening cup means 44 located at the top of 40 and immersed in the slurry. The outer surface of the filter means is permeable to the passage of the slurry liquid therethrough, but not the solid particles in the slurry. The gas bubble and solids reduced slurry liquid passes through the liquid permeable

5   outer surface of the filter means and into its interior as filtrate, which may still possess some gas bubbles and very fine particulate solids. From the interior of means 42, the filtrate then passes down through filtrate conduit and over and up into the lift reactor 30. Not all of the gas bubble-reduced slurry liquid passes through and into the interior of the filter as filtrate. The remaining slurry, now

10   containing a higher concentration of solid particles, continues down through to and out the bottom of downcomer 40, to the lower portion of the slurry body 20 with which it mixes. The flow rate of a gas bubble-reduced slurry down through a vertical downcomer can be substantial and, when used to feed the degassed slurry liquid to the lift reactor, adds to the relatively high flow rate created by the

15   lift action of the hydrogen treat gas injected into the bottom of the hydroisomerizing zone in the lift reactor. In some cases this higher flow rate created by the combination of downcomer and lifting action of hydrogen or hydrogen treat gas will be neither needed nor desired. Therefore, the use of a downcomer to feed the lift reactor is optional and at the discretion of the

20   practitioner. In an experiment with a 30 foot tall slurry hydrocarbon synthesis reactor, using a simple gas disengaging cup on top of a vertical downcomer pipe of the type disclosed in U.S. patent 5,382,748, resulted in a 12 ft/sec liquid flow rate down a 3 inch downcomer pipe, from which only half of the 60 vol. % of gas bubbles had been removed. The liquid entrance 32 of the lift reactor is

25   connected, via hollow fluid conduit 38, to the solids filter 42, located in the interior of vertical downcomer 40. While only one lift reactor and associated downcomer is shown for convenience, a plurality of such reactors and downcomers may be employed in the slurry body. Hollow cup 44, which opens upward in the slurry in which it is wholly immersed, comprises a gas bubble

removal means for removing gas bubbles from the slurry as it flows into the cup and before it flows down the downcomer, and is the type disclosed in the '748 and '468 patents referred to above. Means 44 is wholly immersed in the slurry body and is located in the upper portion of the slurry, to maximize the hydraulic

5   head of the gas bubble reduced slurry entering into 40 and also because the catalyst concentration in the slurry body is typically lowest at the top. Simple baffles 46 located proximate to and spaced apart from the bottom opening of 40 prevent gas bubbles from rising up into the downcomer and impeding the flow of slurry down through it. While only a simple gas bubble removing means 44 is

10   illustrated at the top of the downcomer 40 for the sake of simplicity, it is preferred that both gas bubbles and particulate solids be removed from the slurry, before it passes down through 40. Simple gas and solids disengaging means, such as those disclosed in the '621 and '537 patents referred to above are preferred to means such as conventional filters, magnetic or centrifugal solids

15   separating means, because they do not require pumps or expensive equipment. They also provide a density-difference hydraulic head by virtue of densifying the slurry due to gas bubble removal, to circulate the slurry from the top of the surrounding slurry body down into the downcomer, into and through filter 42, and then up into the lift reactor. As mentioned above, the gas reduced and

20   preferably the gas and solids reduced slurry formed in 44, passes down through conduit 40 and past the solids filter means 42, which separates solids (or additional solids if a solids reducing means is located proximate the top of 40) from the slurry passing down through the interior of the downcomer. Filter means 42 is optional and will not be required if sufficient solids are removed

25   from the slurry by a simple gas bubble and solids removal means referred to above. The hydraulic pressure resulting from removing gas bubbles from the slurry is diminished by the use of a solids filter in the downcomer. A filter support, illustrated as a metal rod 48, supports the filter means in the downcomer and permits the filter to be removed for maintenance and replacement through a

port or conduit 50. A removable plate 54 is detachably attached to 50 via bolts (not shown) that go through flange 52. The gas and solids reduced slurry passing through the filter 42, passes into transfer conduit 38 and up into the interior of lift reactor 30, in which it mixes and reacts with hydrogen in the

5   presence of one or more, and typically more that one monolithic hydroisomerizing catalyst sections or zones 56, which define the hydroisomerization zone. The hydrogen or hydrogen treat gas is injected into the interior of the lift reactor, via multiple hydrogen treat gas injection lines 58, just upstream of each successive downstream catalyst section. Typically and

10   preferably, the hydroisomerization zone comprises a plurality of monolithic catalyst sections or zones, shown as three in the Figure for the sake of illustration. Each section 56 comprises one or more discrete bodies vertically stacked above each other, and vertically spaced apart from neighboring sections to permit the hydroisomerization hydrogen gas injected upstream of each stage,

15   to mix with the upflowing liquid prior to contact with the downstream catalyst section. The hydrogen treat gas provides a lift effect to lift the upflowing liquid through the lift reactor. Multiple injection of the hydrogen treat gas provides mixing of the hydrogen with the upflowing liquid before each of the three hydroisomerization stages shown, and also reduces gas/liquid stratification to

20   less than that which would occur, if all of the hydrogen was injected into the lift reactor at one point. During the hydroisomerization, a portion of the hydrogen is consumed. Also shown in Figure 1 are a plurality of separate, low pressure drop static mixers 68, such as Kenics® static mixers comprising twisted strips of sheet metal, located in the vertical space between each catalyst section. One or more

25   such static mixers is located downstream of each hydrogen injection point and upstream of the next, successive catalyst section to mix and remix the hydrogen gas with the upflowing slurry before it enters the next catalyst section. The hydroisomerized slurry exits out the top 34 of 30, at which point unreacted treat gas and gaseous reaction products separate from the liquid and any particulate

solids, with the liquid and solids passing down into the slurry body 20 with they mix. A support for the catalyst sections and static mixers, illustrated as a metal rod 60, supports the catalyst sections and static mixers in the hydroisomerization zone in the riser reactor 30, and permits them to be removed for maintenance

5 and replacement through a port or conduit 62. A removable plate 64 is detachably attached to 62 via bolts (not shown) that go through flange 66. The extent of the hydrocarbon liquid hydroisomerization per pass through the loop, will vary with the type of catalyst, the amount of catalytic surface area, reaction conditions, hydrogen gas and hydrocarbon liquid flow rate, the amount of

10 residual water and CO, if any, remaining in the liquid, the concentration of normal paraffinic components in the hydrocarbon liquid, etc. The hydrocarbon liquid flowing out of the hydroisomerization reaction zone comprises a mixture of normal paraffins and hydroisomerized components of reduced pour point. If desired, a portion of the upflowing hydroisomerized slurry may be removed

15 from 30 by means not shown and passed out of the synthesis reactor to downstream facilities and processing.

[0016]   It is known that in a Fischer-Tropsch hydrocarbon synthesis process, liquid and gaseous hydrocarbon products are formed by contacting a synthesis

20 gas comprising a mixture of H_2 and CO with a Fischer-Tropsch catalyst, in which the H_2 and CO react to form hydrocarbons under shifting or non-shifting conditions and preferably under non-shifting conditions in which little or no water gas shift reaction occurs, particularly when the catalytic metal comprises Co, Ru or mixture thereof. Suitable Fischer-Tropsch reaction types of catalyst

25 comprise, for example, one or more Group VIII catalytic metals such as Fe, Ni, Co and Ru. In one embodiment the catalyst comprises catalytically effective amounts of Co and one or more of Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts

comprise titania, particularly when employing a slurry hydrocarbon synthesis process in which higher molecular weight, primarily paraffinic liquid hydrocarbon products are desired. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in

5 U.S. patents 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674. Fixed bed, fluid bed and slurry hydrocarbon synthesis processes are well known and documented in the literature. In all of these processes the synthesis gas is reacted in the presence of a suitable Fischer-Tropsch type of hydrocarbon synthesis catalyst, at reaction conditions effective to form hydrocarbons. Some

10 of these hydrocarbons will be liquid, some solid (e.g., wax) and some gas at standard room temperature conditions of temperature and pressure of 25°C and one atmosphere, particularly if a catalyst having a catalytic cobalt component is used. Slurry Fischer-Tropsch hydrocarbon synthesis processes are often preferred, because they are able to produce relatively high molecular weight,

15 paraffinic hydrocarbons when using a cobalt catalyst.

[0017] In a slurry hydrocarbon synthesis process and preferably one conducted under nonshifting conditions, which is the process used in the practice of the invention, the mole ratio of the H_2 to CO in the synthesis gas may broadly

20 range from about 0.5 to 4, but the stoichiometric consumption mole ratio is typically about 2.1/1. The synthesis gas comprising a mixture of H_2 and CO is injected or bubbled up into the bottom of the slurry body in the synthesis reactor, in which the H_2 and CO react in the presence of the particulate Fischer-Tropsch hydrocarbon synthesis catalyst in the slurry liquid, at conditions effective to

25 form hydrocarbons, a portion of which are liquid at the reaction conditions and which comprise the hydrocarbon slurry liquid. The synthesized hydrocarbon liquid is separated from the catalyst particles as filtrate by means such as simple filtration, although other separation means can be used. Some of the synthesized hydrocarbons are vapor and pass out of the hydrocarbon synthesis reactor as

overheads or tail gas, along with unreacted synthesis gas and gaseous reaction products. Some of these overhead hydrocarbon vapors are typically condensed to liquid and combined with the hydrocarbon liquid filtrate. Thus, the initial boiling point of the filtrate will vary depending on whether or not some of the

5 condensed hydrocarbon vapors have been combined with it. Slurry hydrocarbon synthesis process conditions vary somewhat depending on the catalyst and desired products. Typical conditions effective to form hydrocarbons comprising mostly C_{5+} paraffins, (e.g., C_{5+}-C_{200}) and preferably C_{10+} paraffins, in a slurry hydrocarbon synthesis process employing a catalyst comprising a supported

10 cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from about 320-600°F, 80-600 psi and 100-40,000 V/hr/V, expressed as standard volumes of the gaseous CO and H_2 mixture (60°F, 1 atm) per hour per volume of catalyst, respectively.

15 [0018] The hydrocarbons which are liquid at the synthesis reaction conditions and which comprise the slurry liquid which is hydroisomerized by the practice of the invention, are typically fractionated, with one or more of the resulting fractions receiving one or more additional conversion operations. By conversion is meant one or more operations in which the molecular structure of at least a

20 portion of the hydrocarbon is changed and includes both noncatalytic processing (e.g., steam cracking), and catalytic processing in which a fraction is contacted with a suitable catalyst, with or without the presence of hydrogen or other coreactants. If hydrogen is present as a reactant, such process steps are typically referred to as hydroconversion and include, for example, further

25 hydroisomerization, hydrocracking, hydrorefining and the more severe hydrorefining referred to as hydrotreating. Illustrative, but nonlimiting examples of suitable products formed by upgrading include one or more of a synthetic crude oil, liquid fuel, olefins, solvents, lubricating, industrial or medicinal oil, waxy hydrocarbons, nitrogen and oxygen containing compounds, and the like.

Liquid fuel includes one or more of motor gasoline, diesel fuel, jet fuel, and kerosene, while lubricating oil includes, for example, automotive, jet, turbine and metal working oils. Industrial oil includes well drilling fluids, agricultural oils, heat transfer fluids and the like.

[0019]   The invention will be further understood with reference to the Examples below.

EXAMPLES

Example 1

[0020]   Four bifunctional monolithic hydroisomerization catalysts, each consisting of an acidic cracking component and a hydrogenation/dehydrogenation metal component, were prepared using cylindrically shaped and commercially available, open cell alpha alumina foam as the monolith support. The alumina foam cylinders were each 0.5 inches in diameter and 1 inch long. Two different cell sizes were used, one having 20 pores per inch (ppi) and the other having 65 ppi. The average pore sizes were about 1000 μm and 300 μm. Two different zeolites were used as the acidic components, to make two different hydroisomerization catalysts. These zeolites were LZY-82 and zeolite beta. Each zeolite was first impregnated with 0.5 wt. % Pt using standard incipient wetness techniques, dried, and calcined at 400°C for 4 hours. The zeolite materials were slurried in water/acetic acid (5%) and then applied onto the alpha alumina foam as washcoats using multiple dips followed by calcination (600°C for 2 hours). The four finished monolithic catalysts are summarized in Table 1.

Table 1

Catalyst Description	Monolith Volume in.^{3}	Average Loading g/in.^{3}
Pt/beta (20 ppi)	0.196	1.82
Pt/beta (65 ppi)	0.196	1.78
Pt/LZY-82 (20 ppi)	0.196	1.35
Pt/LZY-82 (65 ppi)	0.196	1.67

Example 2

[0021]   These four catalysts were evaluated for their hydroconversion effectiveness for heavy, waxy, paraffinic hydrocarbons using hexadecane (n-$C_{16}H_{38}$) as a representative feed for a Fischer-Tropsch synthesized hydrocarbon liquid. The hydroconversion runs were carried out in a small, up-flow pilot plant running at a hydrogen pressure and nominal treat rate of 750 psig and 2500 SCF/B with weight hourly space velocity (WHSV) ranging from 2.3 to 3.1. The degree of conversion was varied by adjusting the temperature from 400-550°F. Each reactor was charged with 5 of the cylindrical catalytic monoliths in series with alpha alumina foams of similar ppi rating used at the front and back of the reaction zone. The reactor conditions for each run are summarized in Table 2.

Table 2

Feedstock	Hexadecane	Hexadecane	Hexadecane	Hexadecane
Catalyst Description	0.5 wt. % Pt/Beta (20 ppi)	0.5 wt. % Pt/Beta (65 ppi)	0.5 wt. % Pt/LZY (20 ppi)	0.5 wt. % Pt/LZY (20 ppi)
Conditions WHSV, g/hr/g	2.3	2.4	3.1	2.5
Temp., ^{O}F	400-500			
H$_2$ rate, SCF	2500			
Feed, grs/hr	4.1			

[0022]　The results of the runs are shown in Figures 2 and 3. Figure 2 is a plot of hexadecane conversion as a function of temperature, using the Pt/Beta catalysts. Figure 3 is a plot of the selectivity of the hexadecane conversion to C$_{16}$ isoparaffins, determined by gas chromatography, as a function of the reactor temperature for the Pt/Beta catalysts. The results for the Pt/LZY-82 catalysts are not shown, because this catalyst was essentially inactive, even at the relatively high temperature of 550°F. The results for the Pt/Beta catalysts shown in Figure 3 clearly demonstrate the conversion of the hexadecane to isoparaffin. While the cracking activity of the catalysts was greater than desired, the results nevertheless demonstrate the efficacy of hydroisomerizing n-paraffins to isoparaffins, using a monolithic hydroisomerization catalyst.

[0023]　It is understood that various other embodiments and modifications in the practice of the invention will be apparent to, and can be readily made by, those skilled in the art without departing from the scope and spirit of the invention described above. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the exact description set forth above, but rather that the claims be construed as encompassing all of the features of

patentable novelty which reside in the present invention, including all the features and embodiments which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.